

## DESCRIPTION

**Polishing Slurry and Polished Substrate****CROSS-REFERENCE TO RELATED APPLICATION**

This application is an application filed under 35 U.S.C. § 111(a) claiming benefit pursuant to 35 U.S.C. § 119(e)(1) of the filing date of Provisional Application 60/423,376 filed November 4, 2003, pursuant to 35 U.S.C. § 111(b).

**TECHNICAL FIELD**

This invention relates to a polishing slurry used for precision polishing of substrates with optical and electronic applications, such as glass substrates for optical lens, optical disc, magnetic disc, plasma display, liquid crystal display, and LSI photomask. This polishing slurry exhibits excellent polishing properties, namely, has a high rate of polishing and gives a polished surface with a reduced surface roughness and not having surface defects such as scratches to any appreciable extent.

The invention further relates to a process for polishing a substrate with the above-mentioned polishing slurry, a process for producing a polished substrate, and a polished substrate.

**BACKGROUND ART**

In recent years, the importance of high-precision polishing is still more rising in the field of electronics such as a glass substrate for magnetic disc, a glass substrate for liquid crystal display such as thin film transistor (TFT) LCD or twisted nematic (TN) LCD, a color filter for liquid crystal TV, and a glass substrate for LSI photomask.

Especially in the field of substrates for magnetic disc, stiffness and other mechanical strength sufficiently high for use as a substrate rendered thin for weight-saving or for endurance for undulated movement of disc at high speed rotation are required. Further, high recording density is required, and thus, minimization

of floating height of a magnetic head from a magnetic disc substrate is required. For this requirement, it is eagerly desired to provide a mirror-polished surface with a high flatness, an extremely reduced surface roughness, and a minimized number of minute scratches and minute pits. Thus, it is required to polish surface of substrates with highly enhanced precision.

Further, improvements are also being made in chemical composition of glass substrates and a process for making glass substrates for satisfying the requirements for thinning, high mechanical strength and high density recordation. For example, glass substrates other than those made of conventional chemically reinforced glass have been developed, which include crystallized lithium silicate-containing glass substrates, and crystallized glass substrates predominantly comprised of quartz crystal. These glass substrates have very poor processability, and are difficult to polish with conventional abrasive composition at a high polishing rate and with good productivity.

As an abrasive composition for surface polishing of glass substrates, rare earth oxides, especially cerium oxide is used because rare earth oxides exhibit a very high rate of polishing as compared with iron oxide, zirconium oxide and silicon dioxide. Rare earth oxides are used generally as a dispersion of abrasive grains in water or other liquid medium. For surface polishing with an abrasive composition, both of high-precision surface polishing performance and high rate of polishing are required.

For cerium-based abrasive compositions, various proposals have been made to enhance the rate of polishing. For example, polishing techniques using a cerium-based abrasive composition having added therein colloidal silica or alumina, and a cerium-based abrasive composition having added therein magnesium chloride have been proposed (see Japanese Examined Patent Publication No. S38-3643, Japanese Unexamined Patent Publication [hereinafter abbreviated to "JP-A"] No. H3-146585). However, the addition of different kind of sol causes an increase of scratches or pits on a polished surface and hence high surface precision cannot be attained.

Further, in order to achieve high surface precision, an abrasive composition comprised of an alkaline ceric oxide sol

containing an organic acid with at least two carboxyl groups; and a CMP polishing liquid composition comprising cerium oxide particles coated with an anionic surfactant and a nonionic surfactant, and an aqueous dispersion of a surfactant have been proposed (see JP-A H8-3541 and JP-A 2000-248263).

The alkaline ceric oxide sol containing an organic acid with at least two carboxyl groups in the abrasive composition has a small average particle diameter in the range of 2 nm to 200 nm, and hence, the rate of polishing is low, the polishing cost is high, and it is difficult to stably produce a polished substrate with high quality. The above-mentioned CMP polishing liquid inevitably has a low pH value because it contains ceric oxide abrasive grains, and the rate of polishing is low and the surface roughness is large.

Thus, it is impossible to satisfy both of high-precision surface polishing performance and high rate of polishing with any of the hitherto proposed polishing techniques.

#### SUMMARY OF THE INVENTION

In view of the foregoing, a primary object of the present invention is to provide a polishing slurry which satisfies high-precision surface polishing performance and provides a polished surface with a high flatness and a small surface roughness and having minimized number of minute scratches and minute pits, while a high rate of polishing is attained.

In accordance with the present invention, there is provided a polishing slurry comprising an abrasive comprising as a basic ingredient rare earth oxides containing cerium oxide, said polishing slurry further comprising an anionic surfactant and a nonionic surfactant and having a pH value of at least 11. By the term "as a basic ingredient" as used herein we mean that the content is at least 80% by mass.

Preferable embodiments of the above-mentioned polishing slurry are summarized as follows.

The abrasive comprises at least 90% by mass, based on the abrasive, of the rare earth oxides.

The rare earth oxides contain 50% to 90% by mass, based on the rare earth oxides, of cerium oxide.

The rare earth oxides are produced from rare earth carbonate salts as a starting raw material.

The abrasive is comprised of particles having a 50% cumulative average diameter (D<sub>50</sub>) in the range of 0.01  $\mu\text{m}$  to 10  $\mu\text{m}$ .

The abrasive is comprised of particles having a specific surface area in the range of 1  $\text{m}^2/\text{g}$  to 50  $\text{m}^2/\text{g}$ .

The anionic surfactant is at least one kind of surfactant selected from the group consisting of low-molecular-weight compounds and high-molecular-weight compounds, which are selected from carboxylic acid salts, sulfonic acid salts, sulfuric acid ester salts and phosphoric acid ester salts.

The nonionic surfactant is at least one kind of surfactant selected from the group consisting of polyoxyethylene alkyl phenyl ethers, polyoxyalkylene alkyl ethers and polyoxyethylene fatty acid esters.

The polishing slurry further comprises at least one kind of liquid medium selected from the group consisting of water, monohydric alcohols having 1 to 10 carbon atoms, glycols, polyhydric alcohols having 1 to 10 carbon atoms, dimethyl sulfoxide, dimethylformamide, tetrahydrofuran and dioxane.

The polishing slurry further comprises at least one kind of ingredient selected from the group consisting of phosphoric acid esters, cellulose ethers and water-soluble high-molecular-weight compounds.

In accordance with the present invention, there is further provided a substrate which has been polished with the above-mentioned polishing slurry.

The above-mentioned polished substrate is preferably used as a glass substrate for optical lens, a glass substrate for optical disc, a glass substrate for plasma display, a glass substrate for liquid crystal, a color filter for liquid crystal TV, a glass substrate for LSI photomask and a glass substrate for magnetic disc. Of these, a glass substrate for magnetic disc is especially preferable.

#### BEST MODE FOR CARRYING OUT THE INVENTION

The polishing slurry of the present invention comprises (i)

an abrasive comprising as a basic ingredient rare earth oxides containing cerium oxide, (ii) an anionic surfactant and (iii) a nonionic surfactant, and has a pH value of at least 11. By this constitution, the polishing slurry exhibits excellent polishing performance, namely, it gives a polished surface with a highly enhanced flatness, a reduced surface roughness and not having, to any appreciable extent, surface defects such as minute scratches and minute pits, while a high rate of polishing is attained.

If only one of the anionic surfactant and the nonionic surfactant is contained in the slurry, or the slurry has a pH value of lower than 11, at least one of the high-precision surface polishing performance and the high rate of polishing cannot be attained.

The ingredients constituting the polishing slurry of the present invention will be described below.

#### Abrasive

The abrasive used in the present invention comprises at least 80% by mass, preferably at least 90% by mass, based on the abrasive, of rare earth oxides. If the content of rare earth oxides is smaller than 80% by mass, scratches tend to occur on a polished surface.

The rare earth oxides preferably contain 50% to 90% by mass, based on the rare earth oxides, of cerium oxide. With a cerium content of smaller than 50% by mass, the desired high rate of polishing is difficult to attain. In contrast, with a cerium content of larger than 90% by mass, a pH value of at least 11 is difficult to obtain even when an anionic surfactant and a nonionic surfactant are incorporated, with the results that the desired high rate of polishing is difficult to attain and a polished surface is liable to have a large surface roughness.

The rare earth oxides may contain, in addition to cerium oxide, lanthanum oxide, praseodymium oxide, neodymium oxide and other rare earth oxides.

The abrasive is preferably comprised of particles having a 50% accumulative average particle diameter (D<sub>50</sub>), as expressed in terms of volume, in the range of 0.01  $\mu\text{m}$  to 10  $\mu\text{m}$ , more preferably 0.05  $\mu\text{m}$  to 5  $\mu\text{m}$  and especially preferably 0.1  $\mu\text{m}$  to 2.0  $\mu\text{m}$ . When the 50% accumulative average particle diameter (D<sub>50</sub>) is smaller than 0.01  $\mu\text{m}$ , the desired high rate of polishing is difficult to

attain. In contrast, when the 50% accumulative average particle diameter (D50) is larger than 10  $\mu\text{m}$ , a polished surface is liable to have minute scratches and minute pits.

The term "50% accumulative average particle diameter (D50) as expressed in terms of volume" as used herein we mean a particle diameter when the integral of particle diameters reaches 50% as calculated from the smallest diameter to the larger diameter in the particle distribution as expressed in terms of volume.

The rare earth oxides used in the present invention are preferably produced from rare earth carbonate as a starting raw material. The rare earth carbonate used as a starting material is prepared by a process wherein a rare earth concentrate containing large amounts of naturally occurring cerium, lanthanum, praseodymium, neodymium and other rare earth elements is crushed; ingredients other than the rare earth elements, such as alkali metals, alkaline earth metals and radioactive substances, are chemically separated for removal from the crushed product; and ammonium bicarbonate or oxalic acid was added to the rare earth-containing residue to give rare earth carbonate.

The rare earth carbonate is baked at a temperature of about 500°C to about 1,200°C in an electric oven, and the baked product is pulverized whereby a rare earth oxide-based abrasive is obtained. An abrasive having a desired particle distribution can be obtained by appropriately selecting the baking conditions and pulverizing conditions.

The state of baking can be evaluated by the specific surface area of abrasive particles. The specific surface area is preferably in the range of 1  $\text{m}^2/\text{g}$  to 50  $\text{m}^2/\text{g}$ , more preferably 2  $\text{m}^2/\text{g}$  to 20  $\text{m}^2/\text{g}$ . When the specific surface area is smaller than 1  $\text{m}^2/\text{g}$ , minute scratches and minute pits are liable to occur on a polished surface. In contrast, when the specific surface area is larger than 50  $\text{m}^2/\text{g}$ , the rate of polishing is reduced.

#### Anionic Surfactant

The anionic surfactant used in the present invention includes, for example, publicly known carboxylic acid salts such as soaps, N-acylamino acid salts, alkylethercarboxylic acid salts and acylated peptides; sulfonic acid salts such as alkanesulfonic acid

salts (including alkylbenzenesulfonic acid salts), alkynaphthalenesulfonic acid salts, sulfosuccinic acid salts,  $\alpha$ -olefinsulfonic acid salts and N-acylsulfonic acid salts; sulfuric acid ester salts such as sulfated oil, alkylsulfuric acid salts, alkylethersulfuric acid salts, alkylarylethersulfuric acid salts and alkylamidesulfuric acid salts; and phosphoric acid ester salts such as alkylphosphoric acid salts, alkyletherphosphoric acid salts and alkylaryletherphosphoric acid salts. These anionic surfactants may span from low-molecular-weight compounds to high-molecular weight compounds. The salts as herein used are at least one kind of salt selected from Li salts, Na salts, K salts, Rb salts, Cs salts, ammonium salts, and H-type salts.

More specifically, the soaps include fatty acid salts having 12 to 18 carbon atoms, and, as specific examples of the fatty acid groups, there can be mentioned lauric acid, myristic acid, palmitic acid and stearic acid. The N-acylamino acid salts include those which have 12 to 18 carbon atoms, and, as specific examples thereof, there can be mentioned N-acyl-N-methylglycine salts and N-acylglutamic acid salts. The alkylethercarboxylic acid salts include those which have 6 to 18 carbon atoms. The acylated peptides include those which have 12 to 18 carbon atoms. The sulfonic acid salts include those which have 6 to 12 carbon atoms, such as recited above, and, as specific examples of alkanesulfonic acid salts, there can be mentioned laurylsulfonic acid salts, dioctylsuccinosulfonic acid salts, benzenesulfonic acid salts, dodecylbenzenesulfonic acid salts, myristilsulfonic acid salts, kerylbenzenesulfonic acid salts and stearyl sulfonic acid salts. The sulfuric acid ester salts include those which have 6 to 18 carbon atoms, such as recited above, and, as specific examples of the alkylsulfuric acid ester salts, there can be mentioned laurylsulfuric acid salts, dioctylsuccinosulfuric acid salts, myristilsulfuric acid salts and stearyl sulfuric acid salts. The phosphoric acid ester salts include those which have 8 to 18 carbon atoms, such as recited above. High-molecular-weight surfactants include specific polycarboxylic acid type compounds such as "DEMOL EP" (trademark) available from Kao Corporation.

The amount of anionic surfactant is preferably in the range

of 0.05% to 20% by mass, more preferably 0.1% to 10% by mass, based on the abrasive.

Nonionic Surfactant

The nonionic surfactant used in the present invention includes, for example, polyoxyethylenealkyl phenyl ethers, polyoxyethylenealkyl ethers, polyoxyethylene fatty acid esters and polyoxyalkylene-alkyl-ether.

The amount of nonionic surfactant is preferably in the range of 0.0001% to 10% by mass, more preferably 0.001% to 1.0% by mass, based on the abrasive.

The polishing slurry of the present invention can be produced by a process wherein a rare earth oxide-based abrasive, as obtained by baking rare earth carbonate, followed by crushing, is dispersed in a liquid medium such as water or a water-soluble organic solvent, and then, the thus-obtained aqueous slurry is subjected to wet grinding; or a process wherein a rare earth oxide-based abrasive composition, as obtained by baking rare earth carbonate, followed by crushing, is subjected to dry grinding, and then, the thus-obtained powdered abrasive is dispersed in water or a water-soluble organic solvent. However, the former process is preferable wherein the dispersed rare earth oxide-based abrasive is subjected to wet grinding using, for example, a ball mill.

As specific examples of the water-soluble organic solvent, there can be mentioned monohydric alcohols having 1 to 10 carbon atoms such as methanol, ethanol, propanol, isopropanol and butanol; polyhydric alcohols having 3 to 10 carbon atoms such as ethylene glycol and glycerine; and dimethyl sulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran and dioxane. Water, and organic solvents such as alcohols and glycols are preferable. These liquid mediums may be used either alone or as a combination of at least two thereof.

According to the need, to prevent precipitation of the abrasive in the slurry or improve stability of the slurry, a polymeric dispersant such as tripolyphosphate, a phosphoric acid salt such as hexametaphosphate, cellulose ether such as carboxymethyl cellulose, and a water-soluble high-molecular-weight compound such as polyvinyl alcohol can be added in the polishing slurry. These

additive substances may be used either alone or as a combination of at least two thereof. The amount of these substances is preferably in the range of 0.05% to 20% by mass, more preferably 0.1% to 10% by mass, based on the abrasive.

The concentration of abrasive in the thus-prepared polishing slurry is preferably in the range of 1% to 50% by mass, more preferably 5% to 40% by mass and especially preferably 10% to 30% by mass, based on the polishing slurry. When the concentration of abrasive is smaller than 1% by mass, a sufficient polishing performance cannot be obtained. In contrast, when the concentration of abrasive is larger than 50% by mass, the polishing slurry has a high viscosity and its fluidity is lowered, and thus, an excessive amount of abrasive composition is inevitably used for polishing with the result of an increase in polishing cost.

The material or member to be polished with the polishing slurry of the present invention is not particularly limited, but, as examples thereof, there can be mentioned various optical glass materials or members and electronic glass materials or members, such as a glass substrate for optical lens, a glass substrate for optical disc or magnetic disc, a glass substrate for plasma display, a glass substrate for liquid crystal display such as thin film transistor (TFT) LCD or twisted nematic (TN) LCD, a color filter for liquid crystal TV, and a glass substrate for LSI photomask; and general glass articles. The polishing slurry is especially suitable for polishing a glass substrate for magnetic disc.

A glass substrate for magnetic disc has a high stiffness and is capable of being rendered thin, and has a high impact strength. Because of these characteristics, this substrate attracts widespread attention. Glass material of the glass substrate is classified into chemically reinforced glass and crystallized glass. Both of these glass materials have been reinforced to remedy brittleness, which is a defect inherently possessed by glass. Flaws on a glass surface greatly influences the mechanical strength of glass, and therefore, to enhance the reliability of glass, glass is generally chemically reinforced by ion exchange. More specifically, a glass substrate (i.e., original sheet) is immersed in a molten alkali salt to exchange an alkali ion on the glass surface

with an ion of larger size in the molten alkali salt whereby a compression stress-resistant layer is formed on the surface and the breaking strength is greatly enhanced. Elution of an alkali from the inside of glass is suppressed in the chemically reinforced glass. The polishing slurry of the present invention can be used even for polishing the chemically reinforced glass substrate for magnetic disc (HD) with enhanced polishing performance in high polishing rate, reduced roughness of polished surface, and minimized occurrence of minute scratches and other surface defects. As preferable examples of the glass substrate for magnetic disc (HD), there can be mentioned an aluminosilicate glass substrate containing Li<sup>+</sup> and Na<sup>+</sup>, a soda lime glass substrate containing K<sup>+</sup> and Na<sup>+</sup>, and a crystallized glass substrate.

[Examples]

The invention will now be described specifically by the following examples that by no means limit the scope of the invention.

Example 1

4 kg of a commercially available unrefined rare earth carbonate powder (ignition loss: 55.8%) was baked in a box oven. That is, the powder was heated to 900°C at a temperature elevation rate of 1.7°C/minute and maintained at 900°C for 2 hours. The elementary analysis of the baked powder revealed that the content of rare earth oxides was 99% by mass, and the content of cerium oxide was 60% by mass based on the rare earth oxides. The baked powder had a specific surface area of 10 m<sup>2</sup>/g as measured by the BET method.

1.7 kg of the baked powder was put into 2.5 kg of pure water with stirring. Then, 68 g (4% by mass based on the baked powder) of a specific carboxylic acid-type surfactant (tradename "DEMOL EP" available from Kao Corporation) as a carboxylic acid salt (anionic surfactant), and 0.17 g (0.01% by mass based on the baked powder) of polyoxyalkylene alkyl ether (tradename "EMULGEN MS-110" available from Kao Corporation) (nonionic surfactant) were added with stirring to prepare a slurry.

The slurry was subjected to wet grinding while being circulated through a wet mill for 2.5 hours. Then pure water was added to the slurry to give 8 kg of a polishing slurry having an abrasive content of 20% by mass. The polishing slurry had a pH value of

## 12.0.

Particle size distribution was determined on a part of the polishing slurry by a laser diffraction particle size distribution analyzer (HR 850, available from CILAS Co.). The 50% accumulative average particle diameter (D50) as expressed in terms of volume was 0.55  $\mu\text{m}$ .

Examples 2 to 7

Polishing slurries were prepared by the same procedures as described in Example 1 except that the amounts of the carboxylic acid salt (anionic surfactant) and polyoxyalkylene alkyl ether (nonionic surfactant) were varied as shown in Table 1. All other conditions remained the same. The pH values of the slurries are shown in Table 1.

Comparative Examples 1 and 2

Polishing slurries were prepared by the same procedures as described in Example 1 except that the amounts of the carboxylic acid salt (anionic surfactant) and polyoxyalkylene alkyl ether (nonionic surfactant) were varied as shown in Table 1. All other conditions remained the same. The pH values of the slurries are shown in Table 1.

Comparative Example 3

Polishing slurry was prepared by the same procedures as described in Example 1 except that the starting raw material was changed from the commercially available unrefined rare earth carbonate powder to high-purity cerium carbonate, and the amounts of the carboxylic acid salt (anionic surfactant) and polyoxyalkylene alkyl ether (nonionic surfactant) were varied as shown in Table 1. All other conditions remained the same. The pH value of the slurry is shown in Table 1.

Table 1

	Raw material	Amount of anionic surfactant (mass %)*1	Amount of nonionic surfactant (mass %)*1	pH of slurry
Example 1	Rare earth carbonate	4.0	0.01	12.0
Example 2	Ditto	4.0	0.001	11.6
Example 3	Ditto	4.0	0.005	11.7
Example 4	Ditto	4.0	0.05	11.5
Example 5	Ditto	4.0	0.1	12.0
Example 6	Ditto	3.0	0.01	11.2
Example 7	Ditto	10.0	0.01	12.5
Comp.Ex.1	Ditto	4.0	0	11.7
Comp.Ex.2	Ditto	0	1.0	10.1
Comp.Ex.3	High-purity cerium carbonate	10.0	0.01	9.6

Note, \*1 % by mass based on the baked powder

#### Polishing Test

Using each of the polishing slurries prepared in the above examples and comparative examples, a glass substrate was polished under the following conditions.

Polishing machine: 4 way-type both side polisher "USP-5B" available from Fujikoshi Machinery Industries Co.

Polishing pad: Suede-type pad "Polytex DG" available from Rodel Co.

Feed rate of slurry: 60 ml/min

Revolution of base disc: 90 rpm

Polishing pressure: 75 g/cm<sup>2</sup>

Polishing time: 10 min

After polishing, the glass substrate was taken and washed by ultrasonic washing with pure water, and then dried to give a test specimen.

The glass substrate was an aluminosilicate-based glass substrate for magnetic disc with a diameter of 2.5 inches having a surface roughness Ra of 9Å, which was prepared by previously abrading with a commercially available cerium oxide abrasive

compound "SHOROX H-1", tradename, available from Tohoku Kinzoku Kagaku K.K.

Evaluation of Polished Substrate

(1) Surface roughness (Ra)

Surface roughness (Ra) of a glass substrate surface was measured by an atomic force microscope (AFM).

(2) Surface Defect

A glass substrate surface was observed by a differential interference microscope to examine the adhered state on the surface, and occurrence of pits and scratches. Evaluation result of scratches was expressed by the relative number of scratches. Evaluation of surface defects was expressed according to the following three ratings.

A: occurrence of pits was not observed to any appreciable extent and the surface state was good.

B: pits were observed to some extent and the polished substrate was not practically acceptable.

C: surface state was very bad.

(3) Rate of polishing

Rate of polishing ( $\mu\text{m}/\text{min}$ ) was calculated from the weight change of glass substrate as measured before and after polishing.

The evaluation results are shown in Table 2.

Table 2

	Rate of polishing ( $\mu\text{m}/\text{min}$ )	Surface roughness Ra ( $\text{\AA}$ )	Relative number of scratches	Surface defect
Example 1	0.89	2.3	18	A
Example 2	0.79	2.4	30	A
Example 3	0.90	2.3	34	A
Example 4	0.91	2.5	27	A
Example 5	0.81	2.1	33	A
Example 6	0.77	2.6	32	A
Example 7	0.95	2.2	22	A
Comp. Ex. 1	0.47	3.2	39	A
Comp. Ex. 2	0.28	4.1	120	C
Comp. Ex. 3	0.45	4.2	32	A

As seen from Table 2, when polishing was carried out by using the polishing slurries prepared in Examples 1 to 7, the rate of polishing was high, the surface roughness was small, and a good polished surface with no scratches nor surface defects was obtained.

In contrast, when polishing was carried out by using the polishing slurry prepared in Comparative Example 1, which did not contain a nonionic surfactant, the rate of polishing was low and the surface roughness was large.

When polishing was carried out by using the polishing slurry prepared in Comparative Example 2, which did not contain an anionic surfactant and had a pH value smaller than 11, the rate of polishing was low, the surface roughness was large, and scratches and surface defects occurred. This polishing slurry was not suitable for precision polishing.

When polishing was carried out by using the polishing slurry prepared in Comparative Example 3, which contained an anionic surfactant and a nonionic surfactant, but had a pH smaller than 11, the rate of polishing was low, and the surface roughness was large.

#### INDUSTRIAL APPLICABILITY

The polishing slurry of the present invention can be used for polishing various optical glass materials or members and electronic glass materials or members, such as a glass substrate for optical lens, a glass substrate for optical disc or magnetic disc, a glass substrate for plasma display, a glass substrate for liquid crystal display such as thin film transistor (TFT) LCD or twisted nematic (TN) LCD, a color filter for liquid crystal TV, and a glass substrate for LSI photomask; and general glass articles.

The polishing slurry is especially suitable for polishing a glass substrate for magnetic disc, and other substrates used in electronic field. Using the polishing slurry, a highly flat surface with small surface roughness and not having minute scratches and minute pits to any appreciable extent can be obtained at a high polishing rate.